

Synthesis, Characterisation and Dyeing Properties of New Bifunctional Dichloro-s-triazinyl (DCT) Azo Reactive dyes based on 1,4-benzenediamine on Wool Fabrics

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ABSTRACT

Various novel bifunctional azo reactive dyes were synthesized by tetrazotized 1,4-benzenediamine and coupling to various coupling components such as 4-nitroanilino cyanurated H-acids, 4-nitroanilino cyanurated J-acid, 4-nitroanilino cyanurated Laurent acid, 4-nitroanilino cyanurated Tobias acid and 4-nitroanilino cyanurated Gamma acid) respectively. The structures of the synthesized novel bifunctional azo reactive dyes were characterized and confirmed by melting point, FT-IR spectroscopy, FT-IR, ¹H-NMR, MS and UV-visible spectroscopy. The synthesised novel bifunctional azo reactive dyes were applied on wool fabrics under typical exhaustion process and their dyeing properties were evaluated. The percentage exhaustion and percentage fixation of the synthesised dyes on wool fabrics were very good. All the synthesised dyes gave well to excellent properties to washing, light and perspiration respectively.

Keywords: Azo reactive dyes; Bifunctional dyes; Exhaustion; Fixation; Wool fabrics.

1.0. Introduction

Oforghor *et al.*, (2020A) reported that using reactive dyes for dyeing of fabrics have recently led to increased demands on the quality of the dyeing and profitability of the dyeing process. There is still complains on demand for new reactive dyes which have improved properties, especially in respect of application. Barbatu *et al.*, (2011) and Al-Degs *et al.*, (2008) stated that reactive dyes have a sufficient substantively and at the same time a good ease of washing out of the non-fixed portions are required for dyeing. They should furthermore have a good tinctorial yield and high reactivity and dyeing having high degrees of fixing in particular should be produced (Almasian *et al.*, 2015, Kanel *et al.*, (2014). Oforghor *et al.*, (2020B), Khosravi *et al.*, (2005) and Kanethar *et al.*, (2004) reported that reactive dyes, though late entries into the family of synthetic dyes are now a major group of dyes and have suddenly attained a commercial integrity and status. There is no slackening of activity in this field as seen from the large number of patent specification and several ranges which continue to appear in the market (Ali *et al.*, (2014, Patel and Patel, (2012, Cid *et al.*, (2007). Blanco *et al.*, (2016), Alam *et al.*, (2000) and Oforghor *et al.*, (2020A) however, stated that from previous experience of dyeing properties, it can be easily understood that dyes with two reactive groups give a higher fixation yield than dyes with one reactive group, since if one of the two dye-fibre bonds is hydrolyzed, one is still left for fixation. The formation of covalent bond between dyes and fibres had long been attractive to dye chemists, since attachment by physical adsorption and by mechanical obstruction had the disadvantage of either low wash fastness, light fastness, perspiration fastness or high cost (Clark, 2011, Bravo-Diaz, 2010 and Broadbent, 2001). It was obvious therefore, that the covalent bonding of the dye molecules to the fibres would produce very high fastness because covalent bonds are still the strongest known binding forces between molecules (Oforghor *et al.*, 2020B, Patel *et al.*, 2011, Patel and Dixi 2013). Hot-Brand reactive dyes have been widely considered due to their fixation yield on various fibres (Patel *et al.*; (2014) has synthesized bisazo reactive dyes by diazotization of 4,4'-diaminobenzanilide with various cyanurated coupling components. Their dyeing

performance on wool, wool and cotton fibres has been assessed. The dyed fibres showed fair to very good light fastness and very good to excellent washing and rubbing fastness. The present research work is to synthesis, characterisation and dyeing properties of new bifunctional Dichloro-s- triazinyl (DCT) Azo Reactive dyes based on 1, 4-benzenediamine on wool fabrics.

2.0. Experimental

2.1. Materials and Methods

1,4- benzenediamine, Cyanuric chloride, H-acid, J-acid, Laurent acids, Tobias acid, Gamma acid were purchased from Weifang Senya Chemical Company Limited, China. All other chemicals used in this study were of laboratory reagent grade and applied without further purification. The melting points were determined by open capillary method. The UV-visible absorption spectra were recorded using Perkin-Elmer Lambda 25 UV-visible spectrophotometer (at the wavelength of maximum absorption (λ_{max})).

The FT-IR were recorded using (Perkin-Elmer Spectrum RXIFT-IR Spectrometer, ^1H NMR spectra were recorded using (varian 300 MHz Bruker Instrument) and Mass Spectrometer were recorded using Agilent Technologies 5975C VL MSD Mass Spectrometer at the Kharazmi University, Bureau of International Scientific Cooperation, Department of Organic Chemistry, Tehran, Iran.

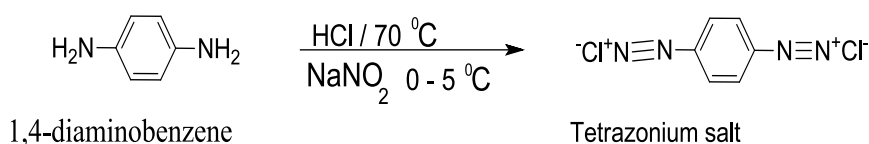
The scoured and bleached wool fabric was obtained from Chemical Processing laboratory, Department of Polymer and Textile Engineering at the Ahmadu Bello University, Zaria. Before dyeing, the fabric was treated with 2% stock concentration of detergent at 60 °C for 30 min, thoroughly washed in water and air dried at room temperature. Applications and evaluation of fastness properties were carried out according to the standard methods in Chemical Processing laboratory, Department of Polymer and Textile Engineering at the Ahmadu Bello University, Zaria.

2.2. Methods

The synthesis of the bifunctional azo reactive dyes involves four (4) steps which are cyanuration of the acids, condensation of the cyanurated acids, tetrazotisation of the intermediates and the coupling of the tetrazotised intermediates with the condensed cyanurated acids (Oforghor et al; 2020)

2.2.1. General procedure for tetrazotization of intermediates

1,4-benzenediamine (0.54g, 0.005mol) was suspended in distilled water (60ml) and hydrochloric acid (0.36g) was added dropwise to the well stirred suspension. The mixture was gradually heated up to 70°C, till clear solution was obtained. The formed solution was gradually cooled to below 5°C in an iced bath, then already cooled (0-5°C) NaNO_2 (0.6g in 4ml H_2O) was added over a period of 30mins with continuous stirring. The stirring was continued for one (1) hour, maintaining the temperature of 0°C-5°C with positive test for nitrous acid with starch iodide paper.

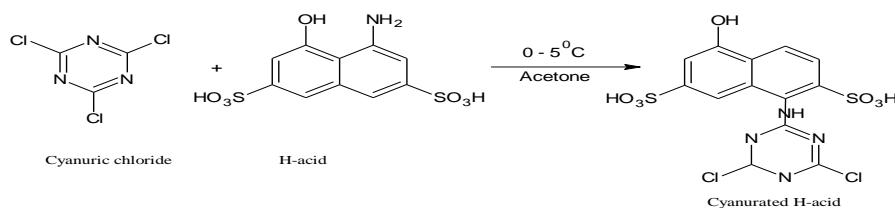


Scheme 1. Tetrazotization of 1,4'-diaminobenzene

After completely destroying the excess of nitrous acid with the required amount of sulphamic acid, the clear tetrazonium solution at 0°C-5°C obtained was used for next coupling reaction. The reaction as shown in the reaction scheme 1 below:

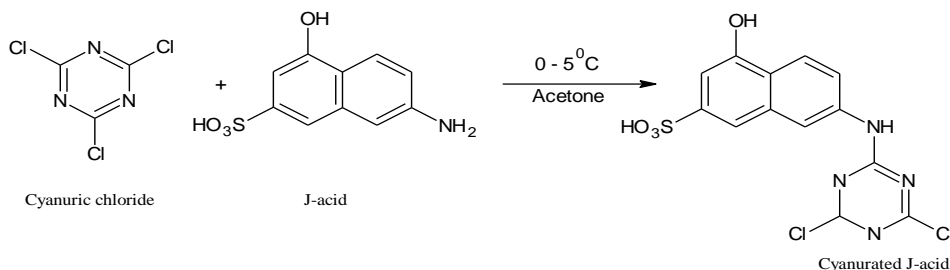
2.2.2. General procedure for cyanuration of the acids

Cyanuric chloride (1.85g, 0.01 mole) was stirred in acetone (25 ml) at a temperature below 5°C for a period of an hour. A neutral solution of H-acid (3.19g, 0.01mole) in aqueous sodium carbonate solution (10% w/v) was then added in small lots about an hour. The pH was maintained neutral by simultaneous addition of sodium carbonate solution (1% w/v). The reaction mass was then stirred at 0-5°C for further 4 hours. The cyanurated H-acid solution was used for subsequent coupling reaction as shown in scheme 2a below:

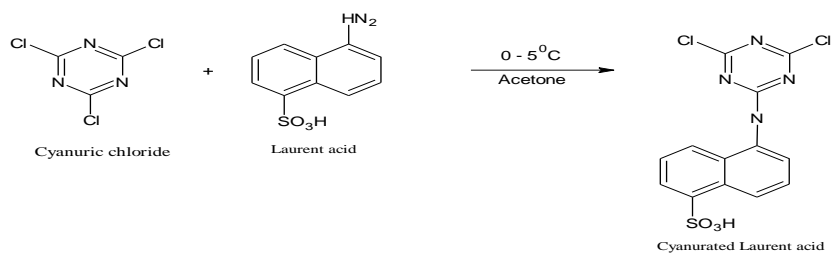


Scheme 2a. Cyanuration of H-acid

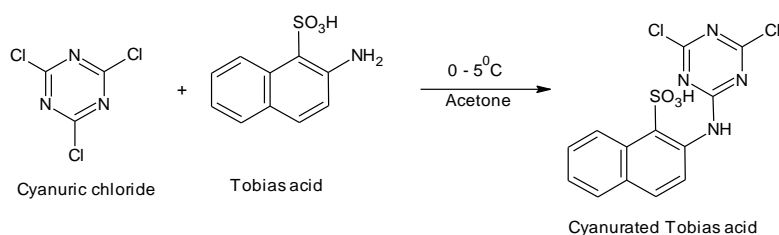
The same procedure (method) was followed to cyanurate J-acid, Laurent-acid, Tobias-acid and Gamma-acid in scheme 2b, 2c, 2d and 2e respectively as shown below.



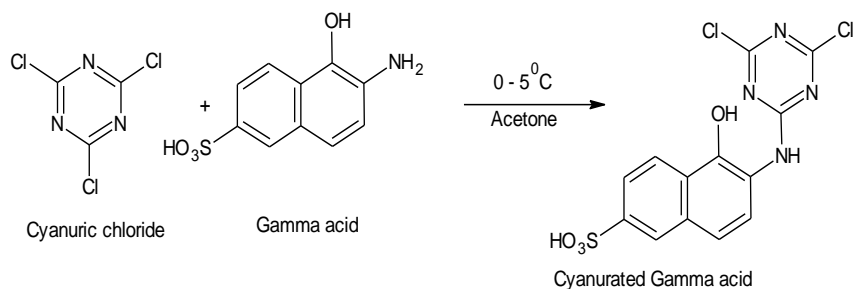
Scheme 2b. Cyanuration of J-acid



Scheme 2c. Cyanuration of Laurent acid



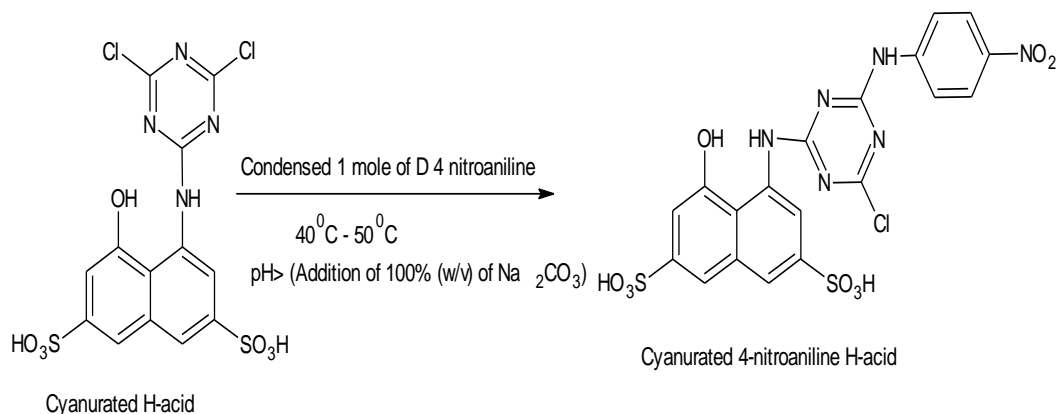
Scheme 2d. Cyanuration of Tobias acid



Scheme 2e. Cyanuration of Gamma-acid

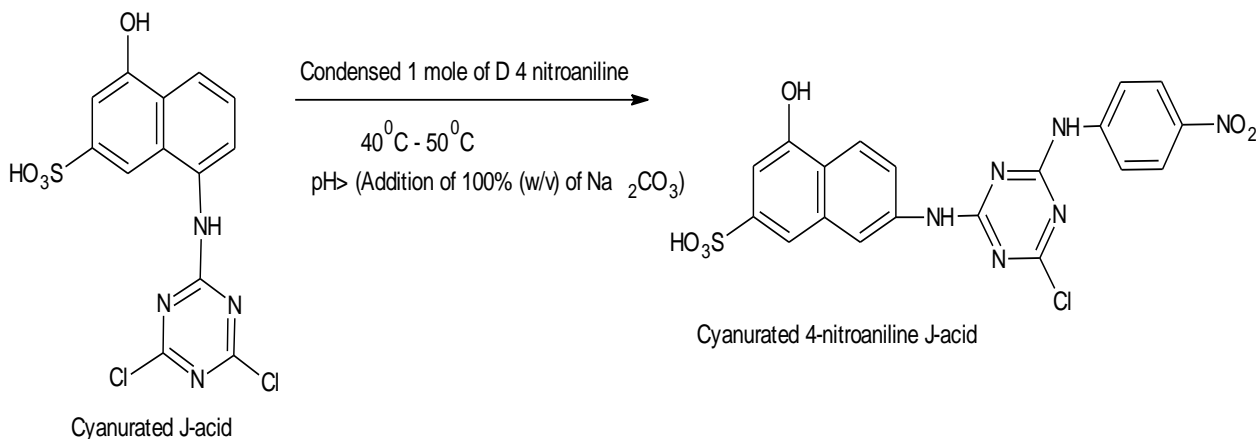
2.2.3. Procedure for condensation of the cyanurated acids

The temperature of ice-cooled well stirred solution of cyanurated H-acid, (4.67 g, 0.01 moles) was gradually raised to 45°C for half an hour. To this cyanurated H-acid, the 4-nitro aniline (1.39 g, 0.01 moles) was added slowly at same temperature, during a period of 30 min, maintaining the pH neutral by simultaneous addition of sodium bicarbonate solution (1% w/v). After the addition was completed, stirring was continued for further 3 hours. The cyanurated 4- nitroanilino H-acid solution thus obtained was subsequently used for further coupling reaction as shown in scheme 1.

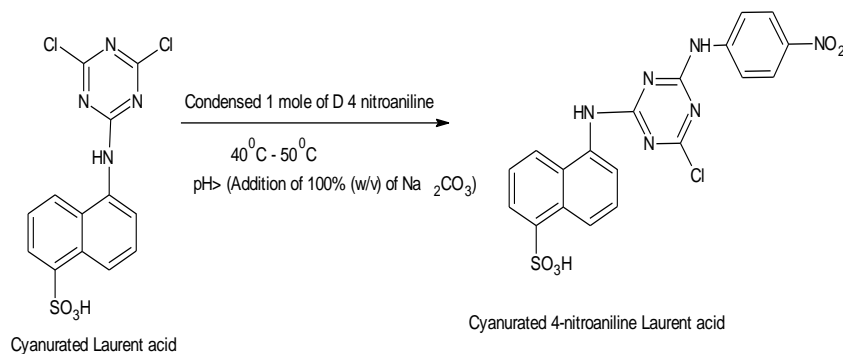


Scheme 3a. Condensation of cyanurated H-acid

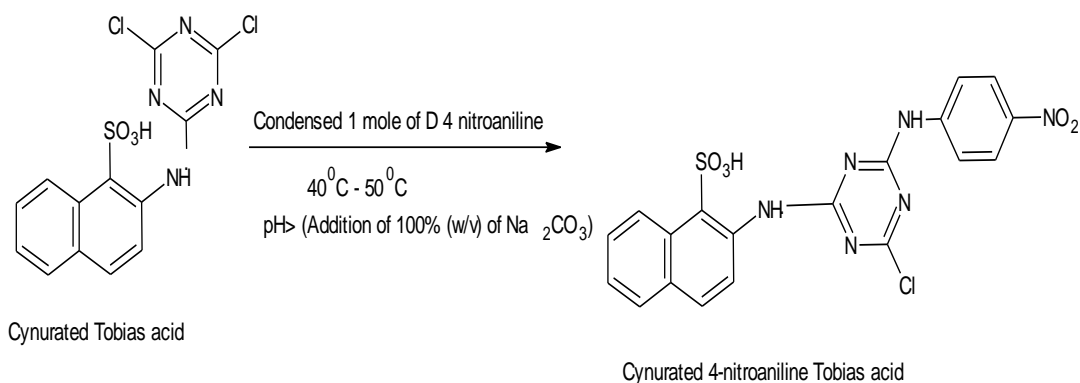
The same procedure (method) was followed for the condensation of cyanurated J-acid, Laurent-acid, Tobias-acid and Gamma-acid in scheme 3b, 3c, 3d and 3e respectively as shown below.



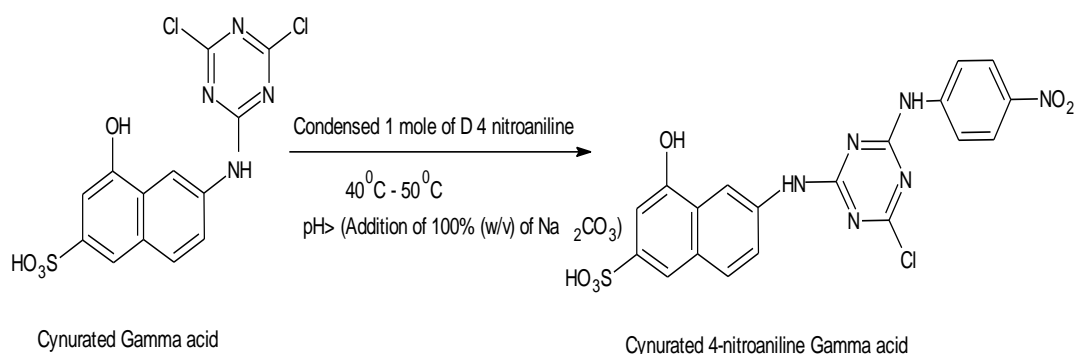
Scheme 3b. Condensation of cyanurated J-acid



Scheme 3c. Condensation of cyanurated Laurent-acid



Scheme 3d. Condensation of cyanurated Tobias-acid

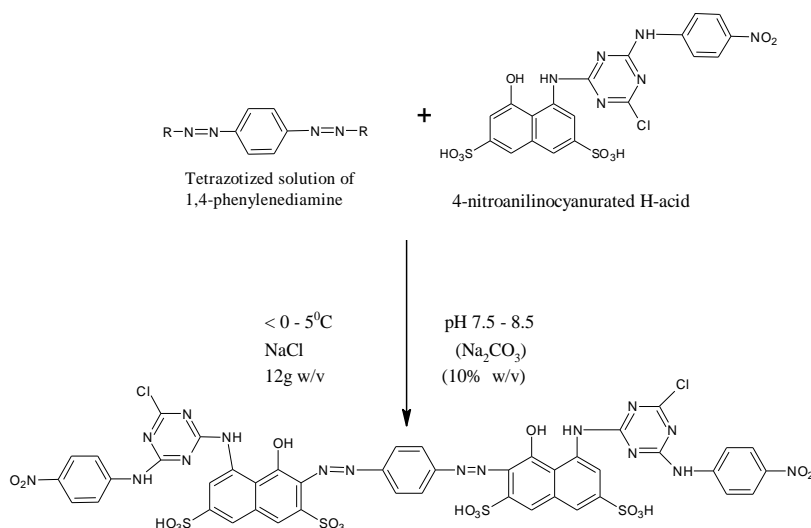


Scheme 3e. Condensation of cyanurated Gamma-acid

2.2.4. Procedure for Synthesis of dye DA₁

The synthesis of DA₁ was done by adding a freshly prepared solution of tetrazotized solution of 1,4-phenylenediamine dropwise over a period of 10 – 20 minutes to the ice-cold and well stirred solution of 4-nitroanilino cyanurated H-acid. The pH 7.5 – 8.5 was maintained by simultaneous addition of sodium carbonate solutions (Na₂CO₃) (10% w/v) where a purple solution was obtained. The stirring was continued to for 3 – 4h at a constant temperature below 0 – 5⁰C for another 1h. The solid violet dye precipitate out and was filtered, washed with little amount of acetone and dried at room temperature with a yield of 87% as shown in the scheme 4a below:

Following the procedure above the other bifunctional dichloro-s-triazinyl (DCT) azo reactive dyes DA₂ (3b), DA₃ (3c), DA₄ (3d) and DA₅ (3e) were synthesised using the various cyanurated coupling components such as J-acid, Laurent acid, Tobias acid and Gamma acid respectively as shown in Table 1. The synthesised dyes were dissolved in minimum amount of DMF, precipitated with acetone and then filtered off (recrystallisation method).



Scheme 4a. Synthesis of dye DA₁

3.0. Dyeing Procedure

3.1. Dyeing of fibres

All the bifunctional dichloro-s- triazinyl (DCT) azo reactive dyes were applied on wool fabrics in 2% shade according to usual procedure (Oforghor *et al.*, 2020). After dyeing, all dyed samples were rinsed with water and air dried.

3.2. Dye exhaustion

The percentage dye exhaustion of the dyed fabrics was evaluated spectrophotometrically using Eqn 1 bellow. The variation in the hues of the dyed fabric results from both the nature and position of the substituent present on the coupler ring. The remarkable degree of levelness after washing indicates good penetration and affinity of these dyes to the fabric.

$$\% E = \left[\left(\frac{C_1 - C_2}{C_1} \right) \right] \times \frac{100}{1} \quad (1)$$

3.3. Dye fixation

The percentage of exhausted dye chemically bound on the fibre, also called total dye fixation ratio (%F), was measured by refluxing the dyed samples in 50% aqueous DMF (liquor ratio 20:1) for 10-15 min to extract the unfixed dye. This procedure was repeated until the extract was clear of the dye solution. The concentration of the extract was then measured spectrophotometrically at λ_{\max} and the dye fixation ratio calculated using Eqn 2

$$\% F = \left[\left(\frac{C_1 - C_2 - C_3}{C_1 - C_2} \right) \right] \times \frac{100}{1} \quad (2)$$

3.4. Fastness properties test

3.4.1. Wash fastness test

The dyed samples were subjected to ISO 3 wash fastness test previously described Oforghor *et al.*, (2020). The change in colour of samples and the staining of the adjacent un-dyed fabric were assessed with appropriate grey scale.

3.4.2. Light fastness test

This was carried out using a Microsal Tester Xenon arc lamp. The dyed samples were cut into 10 cm by 4 cm, placed in the machine and exposed for 48 hrs after which they were removed and the change in colour were assessed using the blue wool scale.

3.4.3. Fastness to perspiration test

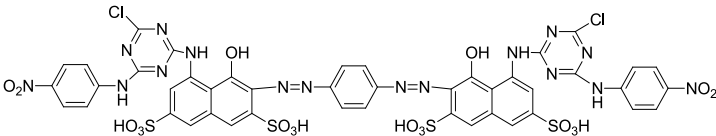
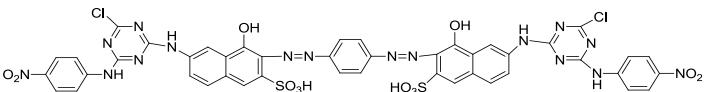
The perspiration fastness of the synthesised dyes were assessed according to the conditions of ISO 105- E04 (1989) previously described Oforghor *et al.*, (2020) for both acidic Perspiration Test and alkaline Perspiration Test

4.0. Results and Discussions

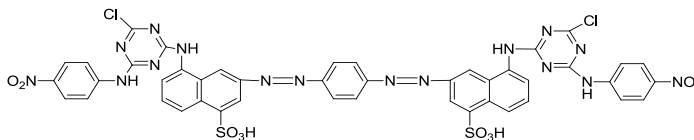
4.1. Synthesis of the bifunctional dichloro-s-triazinyl (DCT) Dyes

Preparation of Tetrazotised solution of 1,4-benzenediamine was done by suspending 1,4-benzenediamine and adding HCl (0.36g) dropwise with continuous stirring and the temperature raised to 70°C till a clear solution is achieved. The temperature lowed to below 0 °C – 5 °C and a solution of already ice cold NaNO₂ was added in small lots over 5 minutes with continuous stirring for 1h maintaining same temperature until a clear solution is achieved as shown in scheme 1. Cyanuration of the acids as shown in Schemes 2a-2e was carried out by stirring cyanuric chloride in acetone at a temperature below 0 °C - 5 °C for an hr, then a neutral solution of H-acid [in aqueous solution of NaCO₃ (10% w/v)] added in small lots over an hr while maintaining a constant pH by adding 1% w/v NaCO₃ at a temperature below 0 °C - 5 °C with continuous stirring for 4h until a clear solution was obtained. In schemes 3a-3e the condensation of the cyanurated acids was carried out by raising the temperature of the ice-cold well stirred cyanurated acids [(H-acid(3a), J-acid(3b), Laurent acid(3c), Tobias acid(3d) and Gamma acid(3e)] gradually to 50 °C over 30 minutes, 4-nitroaniline was added in small lots over 30 minutes while maintaining a constant pH by adding 1% w/v NaHCO₃ with continuous stirring for 5h to obtain the 4-nitroanilino cyanurated acids. The dye DA₁ was synthesised according the route shown in scheme 4a by adding freshly prepared solution of tetrazotised solution of 1,4-benzenediamine dropwise to an ice-cold well stirred of 4-nitroanilino cyanurated H-acid over a period of 10-15 minutes by maintaining pH at 7.5-8.5 by adding NaCO₃ (10% w/v) solution at the same time with continuous stirring for 3-4h at a temperature below 0 °C - 5 °C, after which the dye was precipitated by adding 12g NaCl with continuous stirring for further 1h. The dye filtered, washed and dried at room temperature.

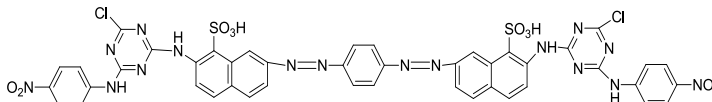
Table 1. Structures and IUPAC names of the synthesized azo reactive Dyes

Dye No.	IUPAC Name	Structures of the Synthesized Bi-functional azo reactive Dyes
DA ₁	3,3'-(1,4-phenylenebis(diazeno-2-1-diyl))bis(5-((4-chloro-6-((4-nitrophenyl)amino)-1,3,5-triazin-2-yl)amino)-4hydroxynaphthene-2,7-disulfonic acid)	
DA ₂	3,3'-(1,4-phenylenebis(diazeno-2-1-diyl))bis(5-((4-chloro-6-((4-nitrophenyl)amino)-1,3,5-triazin-2-yl)amino)-4hydroxynaphthene-2-sulfonic acid)	

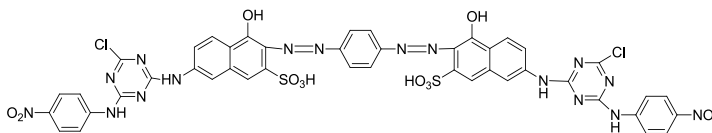
DA₃ 3,3'-(1,4-phenylenebis(diazene-2-1-diyl)bis(5-((4-chloro-6-((4-nitrophenyl)amino)-1,3,5-triazin-2-yl)amino)naphthelene-1-sulfonic acid)



DA₄ 7,7'-(1,4-phenylenebis(diazene-2-1-diyl)bis(2-((4-chloro-6-((4-nitrophenyl)amino)-1,3,5-triazin-2-yl)amino)naphthelene-1-sulfonic acid)



DA₅ 3,3'-(1,4-phenylenebis(diazene-2-1-diyl)bis(7-((4-chloro-6-((4-nitrophenyl)amino)-1,3,5-triazin-2-yl)amino)-4-hydroxynaphthene-2-sulfonic acid)



The physical characteristics of the synthesised dyes are shown in Table 2, it can be seen that the molecular weight of all the synthesized dyes are on the high side. Oforghor *et al.*, (2020) and Patel *et al.*, (2014) reported that high molecular weight dyes exhibit high melting points. This agrees with the literature since most of the synthesized dyes have very high melting point. The shift in λ_{\max} of the synthesised bifunctional azo reactive dyes in different solvents (solvatochromism) is as a result of the solvatochromic effects emanating from changes in dielectric constant of the solvent. The measurement of λ_{\max} in DMF and water indicated that λ_{\max} of the intermolecular charge transfer bonds exhibit a remarkable red shift on transfer from non-polar to polar solvent. This behaviour can be attributed to the polar excited states of the synthesised bifunctional azo reactive dyes are stabilized by polarization interactions forces as the polarisability of the solvent increases (Oforghor *et al.*, (2020) and Abd El- Aal and Koraierm, 2002).

Table 2. Physical Characteristics of the azo reactive dyes

Dye No.	Mol. Wt (g/mol)	Mt. Pt (°C)	Yield (%)	DMF (λ_{\max})	Water (λ_{\max})	ϵ_{\max} in DMF $\times 10^4 \text{ l Mol}^{-1} \text{ cm}^{-1}$
DA ₁	1204.05	310-312	51	530	529	2.07
DA ₂	1106.09	338-340	81	510	510	3.18
DA ₃	1074.10	320-321	50	415	403	8.53
DA ₄	1074.10	315-318	70	413	413	1.69
DA ₅	1106.09	300-302	62	526	516	2.30

The visible absorption maxima of the synthesised bifunctional azo reactive dyes as recorded in Table 2, fall within the visible region (400-700nm) of the electromagnetic spectrum which showed that the synthesised bifunctional azo reactive dyes are colourants with high commercial integrity. The values of the molar extinction coefficient (ϵ) that were determined by Beer-Lambert's law are in the range of $16904.14\text{--}85316.01 \text{ l mol}^{-1} \text{ cm}^{-1}$ which is an indication of high absorption intensity of the synthesised bifunctional azo reactive dyes in DMF respectively. However, the synthesised bifunctional azo reactive dyes have the same chromophoric functionalities, but different in the bridging

groups. The presence of electron donating or electron attracting (withdrawing) groups at the suitable position of the coupler ring affects the absorption characteristics of the synthesised bifunctional azo reactive dyes. Meanwhile, comparing the λ_{max} of the synthesised bifunctional azo reactive dyes DA₁, DA₂, DA₃, DA₄ and DA₅ in DMF showed that their nature of their coupling components (cyanurated 4-nitroanilino H-acid, cyanurated 4-nitroanilino J-acid, cyanurated 4-nitroanilino Laurent-acid, cyanurated 4-nitroanilino Tobias-acid and cyanurated 4-nitroanilino Gamma-acid) are very significant in the context of colour change (Patel et al; 2014). Dye DA₁ was obtained by tetrazotising 1,4 benzenediamine and coupling with cyanurated 4-nitroanilino H-acid which absorbed at 530nm while DA₂ which is obtained by tetrazotising 1,4 benzenediamine and coupling with cyanurated 4-nitroanilino J-acid absorbed at 510nm, hence there was a hypsochromic shift of 20nm. This is attributed to the introduction of additional donor groups onto the coupling component. The coupling of tetrazotised solution of 1,4 benzenediamine with cyanurated 4-nitroanilino Laurent acid yield dye DA₃ which absorbed at 415nm, and there was hypsochromic shift of 125nm when compared to dye DA₁ and hypsochromic shift of 20nm when compared with DA₂. Dye DA₁ was obtained by tetrazotising 1,4 benzenediamine and coupling with cyanurated 4-nitroanilino Tobias acid which absorbed at 413nm while DA₁, DA₂, and DA₃ absorbed at 530nm, 510nm and 415nm which shifted hypsochromically by 127nm, 107nm and 2nm respectively.

Dye DA₁ was obtained by tetrazotising 1,4 benzenediamine and coupling with cyanurated 4-nitroanilino Gamma acid which absorbed at 526nm, hence comparing with DA₁, DA₂, DA₃ and DA₄ there was a hypsochromic shift of 4nm (DA₁), bathochromic shift of 10nm, 111nm, 113nm when compared with DA₂, DA₃ and DA₄ respectively. These observations may be attributed to fact that although the dyes have the same groups but the positions are different, hence for dyes that shifted bathochromically (higher value) they are more place for groups such as NH and SO₃H which cause faster electron oscillation and hence neutralisation of electron faster than dyes with hypsochromic shift (lower value).

Table 3. FT-IR spectra characteristics of the synthesised dyes

Dye no	IR(KBr) cm ⁻¹
DA ₁	3405 (O-H), 3365 (N-H), 2900 (C-H), 1374, 1469 (C-N), 1643 (N=N), 1165, 1060 (S=O), 1595 (N=O), 784 (C-Cl), 841 (SO ₃ H)
DA ₂	3410 (O-H), 3054 (N-H), 2915 (C-H), 1329 (C-N), 1619 (N=N), 1175 (S=O), 1499 (N=O), 765 (C-Cl), 800 (SO ₃ H)
DA ₃	3451 (O-H), 3136 (N-H), 3055 (C-H), 1597 (C-N), 1650 (N=N), 1153, 1072 (S=O), 1515 (N=O), 779 (C-Cl), 840 (SO ₃ H)
DA ₄	3446 (O-H), 3142 (O-H), 3059 (C-H), 1515 (C-N), 1651 (N=N), 1153 (S=O), 1361 (N=O), 779 (C-Cl), 956 (SO ₃ H)
DA ₅	3416 (O-H), 3051 (N-H), 2995 (C-H), 1563 (C-N), 1659 (N=N), 1150 (S=O), 1512 (N=O), 780 (C-Cl), 841 (SO ₃ H)

In general the infra-red spectral of all the dyes DA₁, - DA₅ revealed that O-H showed stretching vibration at 3405-3451 cm⁻¹, N-H showed stretching vibration at 3365cm⁻¹, C=H showed stretching vibration at 2915cm⁻¹, C-N showed stretching vibration at 1515cm⁻¹, 1329cm⁻¹, 1464cm⁻¹, N=N showed stretching vibration at 1651cm⁻¹, S=O showed stretching vibration at 11755cm⁻¹, 1153cm⁻¹ (asym. And sym), N=O showed stretching vibration at 1515cm⁻¹, 1361cm⁻¹, 1335cm⁻¹, C-Cl showed stretching vibration at 779cm⁻¹ and SO₃H showed stretching vibration at 956cm⁻¹ respectively as showed in Table 3.

Table 4. ¹H NMR (500 MHz, DMSO): δH (ppm) Data of the Azo Reactive Dyes

Dye No.	¹ H NMR
DA ₁	1.47(2H, s, -CH ₂), 3.66 (4H, S, -NH), 4.80(2H, S, OH), 7.11 – 8.36 (17H, m, Ar-H), 8.60 (1H, S, SO ₃ H)
DA ₂	1.43 (2H, s, -CH ₂), 3.67 (4H, S, -NH), 4.85(2H, S, OH), 7.06 – 8.41 (19H, m, Ar-H), 8.61 (1H, S, SO ₃ H)
DA ₃	1.43 (2H, s, -CH ₂), 4.66 (4H, S, -NH), 7.06 – 8.42 (20H, m, Ar-H)
DA ₄	1.45 (2H, s, -CH ₂), 3.67 (4H, S, -NH), 7.06 – 8.29 (20H, m, Ar-H)
DA ₅	1.42 (2H, s, -CH ₂), 3.64 (4H, S, -NH), 4.81(2H, S, OH), 7.09 – 8.31 (17H, m, Ar-H), 8.60 (1H, S, SO ₃ H)

The ¹H-NMR spectral for dye DA₁ from Table 4, showed signals (singlet) at 1.42-1.47 δ ppm which confirmed the presence of methylene (-CH) protons, 4.85 δ ppm due to the presence of hydroxyl groups (-OH), 3.66-3.67 δ ppm which confirmed the presence of amino (-NH₂) protons, 7.06-8.42 δ ppm due to the presence of aromatic (Ar-H) protons, 8.60 δ ppm because of the presence of sulphonate group (-SO₃H) groups. The ¹H-NMR spectral for dye DA₂ showed signals (singlet) at 1.42-1.47 δ ppm which confirmed the presence of methylene (-CH) protons, δ 4.85 ppm due to the presence of hydroxyl groups (-OH), 3.67 δ ppm which confirmed the presence of amino (-NH₂) protons, 7.06-8.41 δ ppm due to the presence of aromatic (Ar-H) protons, 8.61 δ ppm because of the presence of sulphonate group (-SO₃H) groups.

The ¹H-NMR spectrum for dye DA₃ showed signals (singlet) at 1.42-1.47 δ ppm which confirmed the presence of methylene (-CH) protons, 3.65 δ ppm due to the presence of amino (-NH₂) protons and 7.06-8.42 δ ppm due to the presence of aromatic (Ar-H) protons. The ¹H-NMR spectral for dye DA₄ showed signals (singlet) at 1.42-1.47 δ ppm which confirmed the presence of methylene (-CH) protons, 3.66 δ ppm which confirmed the presence of amino (-NH₂) protons and 7.06-8.29 δ ppm due to the presence of aromatic (Ar-H) protons.

The ¹H-NMR spectral for dye DA₅ showed signals (singlet) at 1.42-1.47 δ ppm which confirmed the presence of methylene (-CH) protons, 4.81 δ ppm due to the presence of hydroxyl groups (-OH), 3.64 δ ppm which confirmed the presence of amino (-NH₂) protons, 7.09-8.31 δ ppm due to the presence of aromatic (Ar-H) protons, 8.60 δ ppm because of the presence of sulphonate group (-SO₃H) groups.

Table 5. Mass Spectroscopy data of the synthesised azo reactive dyes

Dye No.	Empirical formula	Experimental values of m/z fragment	Corresponding positive charge fragment	Theoretical value
DA ₁	C ₄₄ H ₂₈ Cl ₂ N ₁₆ O ₁₈ S ₄	46.0, 76.0, 106.1, 114.1, 318.1, 1267.2	NO ₂ ⁺ , C ₆ H ₄ ⁺ , C ₃ ClN ₃ ⁺ , C ₆ H ₈ N ₂ ⁺ , C ₁₀ H ₈ NO ₇ S ₂ ⁺ , M	1267
DA ₂	C ₄₄ H ₂₈ Cl ₂ N ₁₆ O ₁₂ S ₂	46.0, 76.0, 106.2, 114.1, 1107.2	NO ₂ ⁺ , C ₆ H ₄ ⁺ , C ₃ ClN ₃ ⁺ , C ₆ H ₈ N ₂ ⁺ , C ₁₀ H ₉ NO ₄ S ⁺ , M	1107
DA ₃	C ₄₄ H ₂₈ Cl ₂ N ₁₆ O ₁₀ S ₂	46.0, 76.0, 106.1, 114.1, 222.1, 1075.1	NO ₂ ⁺ , C ₆ H ₄ ⁺ , C ₃ ClN ₃ ⁺ , C ₆ H ₈ N ₂ ⁺ , C ₁₀ H ₄ NO ₃ S ⁺ , M	1075
DA ₄	C ₄₄ H ₂₈ Cl ₂ N ₁₆ O ₁₀ S ₂	46.0, 76.0, 106.1, 114.1, 222.1, 1075.1	NO ₂ ⁺ , C ₆ H ₄ ⁺ , C ₃ ClN ₃ ⁺ , C ₆ H ₈ N ₂ ⁺ , C ₁₀ H ₉ NO ₃ S ⁺ , M	1074
DA ₅	C ₄₄ H ₂₈ Cl ₂ N ₁₆ O ₁₂ S ₂	46.0, 76.0, 106.1, 114.1, 241.1, 1107.1	NO ₂ ⁺ , C ₆ H ₄ ⁺ , C ₃ ClN ₃ ⁺ , C ₆ H ₈ N ₂ ⁺ , C ₁₀ H ₉ NO ₄ S ⁺ , M	1107

The mass spectral MS for dye DA₁ analysis revealed a fragmentation pattern of NO₂⁺, C₆H₄⁺, C₃ClN₃⁺, C₆H₈N₂⁺, C₁₀H₈NO₇S₂⁺, which indicates molar masses of 46, 76.2, 106.2, 114.1 g/mol respectively. The mass spectrum showed a molecular ion (M⁺) at m/z 1267.2 g/mol and this is in agreement with the molecular mass 1276.1 g/mol of the synthesised dye DA₁. All these differences arise due bridging groups, chromophores, coupling components and reactive systems. The mass spectral MS for dye for dye DA₂ analysis revealed a fragmentation pattern of NO₂⁺, C₆H₄⁺, C₃ClN₃⁺, C₆H₈N₂⁺, C₁₀H₉NO₄S⁺, which indicates molar masses of 46.0, 76.0, 106.2, 114.1 g/mol respectively. The mass spectrum showed a molecular ion (M⁺) at m/z 1107.2 g/mol and this is in agreement with the molecular mass 1107.1 g/mol of the synthesised dye DA₂. All these differences arise due bridging groups, chromophores, coupling components and reactive systems. The mass spectral MS for dye for dye DA₃ analysis revealed a fragmentation pattern of NO₂⁺, C₆H₄⁺, C₃ClN₃⁺, C₁₀H₄NO₃S⁺, C₆H₈N₂⁺, which indicates molar masses of 46.0, 76.0, 106.1, 114.1, 222.1 g/mol respectively. The mass spectrum showed a molecular ion (M⁺) at m/z 1075.1 g/mol and this is in agreement with the molecular mass 1075.1 g/mol of the synthesised dye DA₃. All these differences arise due bridging groups, chromophores, coupling components and reactive systems. The mass spectral MS for dye for dye DA₄ analysis revealed a fragmentation pattern of NO₂⁺, C₆H₄⁺, C₃ClN₃⁺, C₁₀H₉NO₃S⁺, C₆H₈N₂⁺, which indicates molar masses of 46.0, 76.0, 106.1, 114.1, 222.1 g/mol respectively. The mass spectral showed a molecular ion (M⁺) at m/z 1075.1 g/mol and this is in agreement with the molecular mass 1075.2 g/mol of the synthesised dye DA₄. All these differences arise due bridging groups, chromophores, coupling components and reactive systems. The mass spectral MS for dye for dye DA₅ analysis revealed a fragmentation pattern of NO₂⁺, C₆H₄⁺, C₃ClN₃⁺, C₆H₈N₂⁺,

$C_{10}H_9NO_4S^+$, which indicates molar masses of 46.0, 76.0, 106.1, 114.1, 241.1 g/mol respectively. The mass spectrum showed a molecular ion (M^+) at m/z 1107.1 g/mol and this is in agreement with the molecular mass 1107.2 g/mol of the synthesised dye DA₅. All these differences arise due bridging groups, chromophores, coupling components and reactive systems.

Table 6. Exhaustion and fixation study of the azo reactive dyes

Dye No	Shade on wool	Exhaustion (%)	Fixation (%)
		Wool	Wool
DA ₁	Light brown	75	96
DA ₂	Light orange	69	92
DA ₃	Yellow	71	92
DA ₄	Light orange	81	86
DA ₅	Yellow	68	91

The percentage exhaustion of 2% dyeing on wool fabric showed from 65.67% to 78.99%, for wool fabric showed from 65.41% to 76.46% and for cotton fabric showed from 66.02% to 75.98%. The percentage fixation of 2% dyeing on wool fabric showed from 70.39% to 93.78 %, for wool fabric showed from 75.97% to 92.90% and for cotton fabric showed from 73.39% to 95.31 %, (Table-3).

Table 7. Fastness performance properties of the azo reactive dyes

Dye No	Wash fastness	Light fastness	Perspiration fastness	
			Alkaline	Acidic
	Wool	Wool	Wool	Wool
	Cc	Cc	cc	Cc
DA ₁	4-5	6	3-4	3-4
DA ₂	4	4	4	4
DA ₃	4	4	3-4	3-4
DA ₄	4	5	3	4
DA ₅	4	5	4	3-4

cc=colour change

Fastness properties to washing: 1-poor, 2-moderate, 3-fair, 4-very good, 5-excellent;

Fastness properties to light: 1-poor, 2-slight, 3- moderate, 4- fair, 5- good, 6- very good;

Fastness properties to perspiration – alkaline and acidic: 1-poor, 2-fair 3-good, 4-very good.

The data for the fastness properties to washing (IS 765-1979 (Patel et al, 2011), fastness properties to light (BS: 1006-1978 (Oforghor *et al.*, 2020B, Patel et al, 2011) and fastness properties to perspiration – alkaline and acidic (Kkhaeai et al, 2013) are recorded in Table 4. From the result the fastness properties to washing, fastness properties to light and fastness properties to perspiration – alkaline and acidic showed very good performance.

5.0. Conclusion

New bifunctional dichloro-s-triazinyl (DCT) azo reactive dyes based on 1, 4-benzenediamine has been successfully synthesised. 1,4-benzenediamine was tetrazotized and coupled with cyanurated 4-nitroanilino R' acids (H-acid, J-acid, Laurent acid, Tobias acid and Gamma acid) coupling components to give the corresponding bifunctional dichloro-s-triazinyl (DCT) azo reactive dyes (DA₁-DA₅). These dyes gave pink, orange, brown and yellow shade on wool fabrics. The dyes gave better light fastness and seem to have good dyeing performance on wool fabrics. The exhaustion and fixation performance of these dyes are very satisfactory. The remarkable degree of levelness after washing indicates the good penetration and affinity of the dyes to wool fabrics.

Declarations

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Competing Interests Statement

Authors have declared no competing interests.

Consent for Publication

The authors declare that they consented to the publication of this study.

References

- Ali, S., Khatri, Z., Khatri, A., Tanwari, A. (2014). Integrated desizing-bleaching-reactive dyeing process for cotton towel using glucose oxidase enzyme. *J. Clean. Prod.*, 66: 562–567.
- Alam, M.S., G.A. Khan, S.A. Razzaque, M.J. Hossain, M. Minhaz-ul-Haque and S. Zebsyn (2000). Dyeing of cotton fabrics with reactive dyes and their physico-chemical properties. *Indian Journal of Fibre & Textile Research*, 33: 58–65.
- Al-Degs, Y.S., El-Barghouthi, M.I., El-Sheikh, A.H., Walker, G.M. (2008). Effect of solution pH, ionic strength, and temperature on adsorption behavior of reactive dyes on activated carbon. *Dyes Pigment.*, 77: 16–23.
- Almasian, A., Olya, M.E., Mahmoodi, N.M. (2015). Synthesis of polyacrylonitrile/polyamidoamine composite nanofibers using electrospinning technique and their dye removal capacity. *J. Taiwan Inst. Chem. Eng.*, 49: 119–128.
- Barbatu, A., I.C. Stancu, R.-A. Mitran and Ş. Tomas (2011). Reactive dyes based on 2, 4, 6-trichloro-pyrimidine-5-carbaldehyde anchor group. *UPB Sci. Bull. Series B*, 73(4): 135–142.
- Blanco, S.P.D.M., Scheufele, F.B., Módenes, A.N., Espinoza-Quñones, F.R., Marin, P., Kroumov, A.D., Borba, C.E. (2016). Kinetic, equilibrium and thermodynamic phenomenological modeling of reactive dye adsorption onto polymeric adsorbent. *Chem. Eng. J.*, 307: 466–475.

- Bravo-Díaz, D.C. (2010). Diazohydroxides, Diazoethers and Related Species. in Rappoport, Zvi (ed.), *PATAI's Chemistry of Functional Groups*, John Wiley & Sons, Ltd.
- Broadbent, A.D. (2001). Basic principles of textile coloration, Bradford Society of Dyers and Colorists West Yorkshire, Pages 268(5).
- Cid, M.V.F., Spronsen, J.V., Kraan, M.V.D., Veugeler, W.J.T., Woerlee, G.F., Witkamp, G.J. (2007). A significant approach to dye cotton in supercritical carbon dioxide with fluorotriazine reactive dyes. *J. Supercrit. Fluid*, 40: 477–484.
- Clark, M. (2011). Fundamental principles of dyeing, *Handbook of Textile and Industrial Dyeing: Principles, Processes and Types of Dyes*, 1: 1.
- Kamel, M.M., Y. Youssef, N. Ali and S.A.A. El Megiede (2014). Synthesis and application of novel bifunctional pyrazolo [1, 5-a] pyrimidine reactive dyes. *Int. J. Curr. Microbiol. App. Sci.*, 3(10): 519–530.
- Kanetkar, V., G. Shankarling and S. Patil (2000). Recent developments in reactive dyes part 1: Introduction and bifunctional reactive dyes. *Colourage*, 47(3): 35–46.
- Khazaei, Ardeshir, Kazem-Rostami, Masoud, Zare, Abdolkarim, Moosavi-Zare, Ahmad Reza, Sadeghpour, Mahdieh, Afkhami, Abbas (2013). Synthesis, characterization, and application of a triazene-based polysulphone as a dye adsorbent. *Journal of Applied Polymer Science*, 129(6): 3439–3446. doi: <https://doi.org/10.1002%2Fapp.39069>.
- Khosravi, A, Moradiam, S, Garanjig, K and Taromi, F.A. (2005). Synthesis and characterization of some monoazo disperse dyestuffs based on Naphthalimide Derivatives for dyeing polyester. *Journal of the Chinese Chemical Society*, 52: 495–502.
- Oforghor, A.O, K.A Bello, M.K. Yakubu and Nkeonye, P.O. (2020A). Synthesis, Characterisation and Dyeing Properties of Novel Bifunctional Sulphatoethylsulphone (SES) Azo Reactive Dyes Based On 1, 4-Diphenylenediamine. *NSUK Journal of Science and Technology (NJST)*, 7(1&2): 76–82.
- Oforghor, A.O, K.A Bello, M.K. Yakubu and Nkeonye, P.O. (2020B). Synthesis, Characterisation and Dyeing Properties of New Bifunctional Dichloro-S-Triazinyl (DCT) Azo Reactive Dyes Based On 1,4-Diphenylenediamine. *NSUK Journal of Science and Technology (NJST)*, 7(1&2): 19–25.
- Patel, D.R and Patel Keshav C. (2012). *Journal of Saudi Chemical Society*.
- Patel, D.R, et al. (2011). Colorimetric studies of some newly synthesized bisazo reactive dyes. *Arabian J. of Chem.*
- Patel, D.M, Patel, T.S and Dixi, B.C. (2013). Synthesis, characterization and dyeing performance of new bisazo–bisazomethine disperse dyes. *Journal of Saudi Chemical Society*, 17(2): 203–209.
- Patel, J.R, Patel, M.H Pranav, S and Mallika, S.S. (2013). Effect of domestic laundering on color fastness of three newly synthesized reactive dyes on 100% cotton fabric. *Indian Journal of Science*, 4(11): 68–75.
- Patel, J.R, Patel, M.H, Shrivastav, P.S and Sanyal, M. (2014). Standardization of variables for dyeing cotton fabric with five synthesized reactive dyes. *J. Phy. Chem. Sci.*, 1: 1–7.